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LOW COST ORGANIC MODERATOR-COOLANTS FOR NUCLEAR REACTORS

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**NATIONAL REACTOR TESTING STATION
US ATOMIC ENERGY COMMISSION**

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LOW COST ORGANIC MODERATOR-COOLANTS FOR NUCLEAR REACTORS

SUMMARY

Two sources of promising low cost coolants for nuclear power reactors were found: heavy cycle oils from catalytic cracking of heavier petroleum fractions, and coal tar oil. The former required hydrodesulfurization and hydrodealkylation for satisfactory radiolytic and thermal stability. The latter was already very lightly alkylated and radiolytically stable but required hydrodesulfurization for satisfactory thermal stability. The present commercial worth of the raw stocks is about one cent a pound. Refining should not raise their cost above five cents a pound if done on a commercial scale. This compares well with the present price of terphenyl (17¢/lb).

The refined coolants resembled terphenyl in boiling range, density, viscosity, and proton density. They generated from 0.5 to 0.8 the polymer generated by terphenyl in simultaneous irradiations at 650°F under 6-MeV electrons for eight hours or a total dose of about 6×10^9 rads. The refined coolants generated from 1-1/2 to 30 times as much gas (mainly hydrogen) as generated by terphenyl. Even at the highest rate the loss of coolant was negligible. The refined coolants begin to decompose thermally at 750°F, about 50°F lower than terphenyl. The new coolants have been tested only in static systems but promise sufficient reduction in coolant costs that they should be tested in in-pile loops when needed.

The source of the stocks from which the coolants were made appeared to have little effect on their stability. The degree of alkylation of the condensed aromatic rings is limited by their stability. The more stable coolants contained on an average from 0.3 to 0.5 methyl group per molecule and from 0.04 to 0.3 higher alkyl group averaging two carbons in length per molecule. Phenanthrene appeared to be the dominant ring system with some anthracenes indicated in the coolant from coal tar and some pyrene in the petroleum-based coolant.

LOW COST ORGANIC MODERATOR-
COOLANTS FOR NUCLEAR REACTORS

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LOW COST ORGANIC MODERATOR-COOLANTS FOR NUCLEAR REACTORS

I. INTRODUCTION

The objective of this investigation was to find a substitute for terphenyl as a nuclear reactor coolant-moderator which would be much lower in cost, yet possessing adequate thermal and radiation stability. A reduction in the net cost of replacement of decomposed coolant could be achieved even though the decomposition rate of the new coolant was higher than that of terphenyl. Operability of the reactor, and supply problems, however, will set a practical maximum to the tolerable decomposition rate.

Two obvious sources of low cost organic fluids approximating the necessary physical properties immediately suggest themselves - coal tar distillates and heavy aromatic petroleum fractions. Extensive work on stability of hydrocarbon types has shown that the composition of these materials includes some of the more stable compounds. Some prior work indicated possibilities for a few oils and tars; the importance of the possible cost savings is so great that it appeared worthwhile to extend the area of investigation. Moreover, marked changes in uses and demand for hydrocarbons in the last several years have caused changes in petroleum processing. In particular, there are now being produced many fractions rich in the aromatics and condensed ring systems which have been shown to be very resistant to radiation. New analytical methods are just making known information on the composition of these materials far beyond that available a few years ago. It therefore seemed profitable to institute a new and thorough survey of such currently available low cost liquids.

In this current survey, promising materials were found; but, these materials were not sufficiently stable as received to be serious competitors to terphenyl. However, the value of the fractions is so much below that of terphenyl that the cost of one or more processing steps probably may be added. Accordingly, studies have been included in which such operations as desulfurization, dealkylation, etc, were applied to the original materials. Very promising leads were found in such studies, but the termination of the contract work severely limited the scope of the studies.

II. BACKGROUND AND PREVIOUS WORK

This research is based on and starts from three earlier and related areas of study: (a) a few reported studies on materials of this sort by other contractors, (b) reported studies on the radiation and thermal stability of pure hydrocarbons and hydrocarbon classes, and (c) information on the types and individual molecular species found by modern analytical techniques in the fractions available. Additional information became available after the start of the studies, from this laboratory's proprietary work in other areas, and from work of other AEC contractors which was important to, and was used to modify plans as the work progressed.

1. STUDIES BY OTHERS ON LOW COST COOLANTS

While a few scattered tests were made in very early surveys and some information was available from private radiation research of industrial firms, only one or two direct attacks had been reported on this problem. Prior to 1960, Atomics International had studied a few industrial materials, which they had invited various firms to submit, and had found one, which was at that time designated as "alkylphenanthrene", to be interesting [1, 2]. Further work was done later on this petroleum fraction, then designated by Atomics International as "condensed polycyclic coolant" [3,4], and on a few other materials, especially coal tar products [4]. The petroleum fraction had been prepared for Atomics International by Humble Oil and Refining Co. It was reported by Humble to be a refinery fraction which had received some further processing (probably desulfurization) and was officially designated by them as "Humble Nuclear Reactor Coolant No. 1 (Low Sulfur)" [5] and this designation will be used in this report in place of the earlier names used by Atomics International.

California Research Corp. carried out a study of a number of their available heavy oils [6] and more recently resumed some research in this area [7]. No very specific conclusions were presented in the verbal report, which is all that has been made available to Phillips Petroleum on the early tests. Monsanto Chemical Co. also has reported verbally [8] that a survey was made of low cost industrial materials which might compete with their Santowax terphenyl mixture, but no data has been published on it. Esso Research and Engineering Co. reviewed the field of low cost petroleum coolants thoroughly in 1959 [9].

2. STABILITY OF AROMATIC HYDROCARBON CLASSES

Rather extensive studies have been made on the stability of organic hydrocarbons to radiolytic and thermal degradation. One of the most thorough studies of this nature, on radiolytic breakdown at elevated temperatures, was made by West and coworkers at California Research Corp. [10]. This group determined the threshold temperatures for rapid thermal decomposition for a wide variety of hydrocarbons. A rather sharp inflection in the curve of damage rate vs temperature was noted. This temperature was 745°F for perylene, 750°F for pyrene, 765°F for chrysene, and 810 to 840°F for naphthalene. Polyphenyls were somewhat higher, about 855 to 860°F. These results are typical, and indicate

that condensed ring aromatics offer possibilities as coolants, especially if operating temperatures in the nuclear reactors do not need to exceed 750°F. Thus, if materials are available industrially which very largely contain such systems, some hope for development of low cost coolant exists.

3. COMPOSITION OF PETROLEUM AND COAL TAR MATERIALS

The demonstrated maximum stability of the polyphenyls and condensed ring aromatics indicates that the search for low cost industrial materials should center on materials of this composition, if known. No sources containing appreciable amounts of the most desirable compounds, the polyphenyls, is known. Condensed ring polycyclics on the contrary are well known to be the major constituents of high boiling coal tar fractions. Naphthalene is produced from the light oil; the middle oils, often actually called "anthracene oil", serve as commercial sources of anthracene and phenanthrene. Other condensed aromatics are recoverable from the heavier oils. Selected, purified fractions of coal tar middle oils, particularly those rich in phenanthrene rather than anthracene, certainly should be studied.

Petroleum refineries have a number of types of materials which have approximately the same molecular weight and boiling range. These include distillate fractions, lubricating oils, catalytic cracking cycle oils, etc. Paraffinic and naphthenic types are present in major proportions in some of these, which would therefore be expected to be of low stability. But in others from certain crude sources, or from certain refining processes, aromatics reach high percentages, and stable materials might be hoped for. The condensed ring aromatics are resistant to cracking, and so concentrate in the cycle oils. Analyses of these and other petroleum fractions show that phenanthrenes, anthracenes, naphthalenes, pyrenes, and other condensed ring aromatics are present in these cycle oils [11, 12].

Modern refining methods have tended to concentrate these hydrocarbons in the resistant residues. Since the concentration is essentially by hydrocarbon type, the composition of the residues from various crudes and different refineries will contain the same materials. The crude source and exact process used will influence primarily the quantity produced, and perhaps the dilution with some other materials. Such fractions should therefore have a wide availability.

Recently, some demands have developed for these highly aromatic materials, and modern refining processes have been applied to produce them. Solvent extraction in particular is used in many refineries to produce such fractions [11, 12]. They are in particular demand as feedstocks for the furnace processes of producing carbon black. The availability of these liquids justifies reopening the survey of petroleum stocks.

III. MATERIALS AND METHODS

1. HYDROCARBON STOCKS

Hydrocarbon stocks must be potentially available in large volume at low cost and possess approximately the desired vapor pressure and viscosity characteristics. In most cases the criterion of high aromaticity was also applied in the selection. The materials as originally assembled fell into the following groups.

1.1 Petroleum Refining Cycle Oil

These materials, variously designated by different refiners as "cycle oils", "slurry oils" or "decant oils", represent the recycled, unconverted materials from catalytic cracking processing of heavy oil fractions, eg, gas oils, reduced crudes, etc. These materials, therefore, represent the more resistant hydrocarbons in the original oils. These are the aromatic and condensed ring compounds as is well known from work such as carried out in the Organic Reactor Program, as well as from analytical evidence available to the petroleum industry. The samples in some cases represent first recycle streams. In the cases of those streams designated slurry or decant oils, these represent the final very heavy, semi-solid streams discarded from the units and contain hydrocarbons which have resulted from cracking or have been formed after many passes through the process.

Most of the materials were obtained from various Phillips refineries. These materials represent, however, a wide variety of crude oil sources and some variations in refining processes. The materials are representative, but not a complete sampling of materials available in the United States.

1.2 Aromatic Fractions and Extracts

These are fractions prepared especially for high aromatic content, and were made originally in most cases for evaluation as feed stocks for carbon black manufacture by the furnace process. Fractionation, solvent extraction, and other refining processes have been applied to the original heavy petroleum oils. Samples included in this group were prepared by a number of different U. S. refining companies, and had been submitted for evaluation for carbon black feeds or other purposes. In general, no indication has been given of the refining process used, but where operations other than fractional distillation have been employed, it is believed it has usually been extraction with a solvent selective for aromatics.

The material designated "Borger SO₂ extract oil" is an oil produced by extraction of aromatics from a heavy cycle oil by liquid sulfur dioxide, in Phillips' (Borger, Texas) refinery. Some samples of this material were re-extracted in the laboratory, using dimethyl sulfoxide.

1.3 Humble Nuclear Reactor Coolant (Low Sulfur)

This is material of petroleum origin prepared by Humble Oil and Refining Co. in their Baytown, Texas refinery. It was evaluated first by Atomic International. Humble then prepared a 65-gallon batch for further evaluation. It was divided between a 55-gallon drum submitted to Atomic International for test

TABLE I
STOCKS FROM REFINERIES OF PHILLIPS PETROLEUM COMPANY

Source/Stock	API ⁽¹⁾	BMCI ⁽²⁾	Visco- sity, cs at 210°F	Vacuum Distillation Fractions With End Points Of:							
				600°F		700°F		800°F		900°F	
				%	RI 75°C	%	RI 75°C	%	RI 75°C	%	RI 75°C
<u>Kansas City</u>											
Heavy cycle oil	26.4	--	-	10	1.549	52	1.595	81	1.65	92	1.681
Decant oil	11.9	83	4.6	12	1.499	23	1.546	62	1.554	--	--
<u>Borger, Texas</u>											
Heavy cycle oil	33.5	35		9	1.469	73	1.460	96	1.469	--	--
Decant oil	23.4	49		--	--	21	1.480	71	1.501	--	--
SO ₂ extract oil	11.3	91	2.7	30	1.528	72	1.567	--	--	--	--
DMSO extract of SO ₂ extract	2.7	--	-	4	1.549	52	1.595	81	1.645	92	1.681
<u>Woods Cross, Utah</u>											
Synthetic tower bottoms	7.7	--		--	--	18	1.535	57	1.563	83	1.659
<u>Great Falls, Montana</u>											
Slurry oil	--	--	-	44	1.520	79	1.540	92	1.543	98	1.552
<u>Okmulgee, Oklahoma</u>											
Decant oil	9.3	94	4.0	--	--	36	1.551	72	1.573	--	--

(1) API gravity.

(2) Bureau of Mines Correlation Index of Aromatic Content = $\frac{67030}{131.5 + \text{API}} - 456.8 + \frac{87553}{\text{Avg. BP}(^{\circ}\text{R})}$

TABLE II
STOCKS FROM OTHER SOURCES

Source/Stock	API	BICI	Viscosity Temp. °F		Vacuum Distillation Fractions With End Points Of:							
					600°F		700°F		800°F		900°F	
			SUS	OF	%	RI 75°C	%	RI 75°C	%	RI 75°C	%	RI 75°C
<u>Esso, Baton Rouge</u> Aromatic concentrate	3.0	110	117	175	--	--	25	1.586	51	1.610	73	1.616
<u>D-X Sunray, Tulsa</u> Aromatic concentrate	3.0	111	72	210	--	--	--	--	32	1.569	67	1.638
<u>Cities Service, Lake Charles</u> Aromatic concentrate	3.4	114	47	210	4	1.492	22	1.548	52	1.608	74	1.647
<u>Pittsburgh Chemical</u> Coal tar distillate	3.2	101	<u>CS</u> 11	200	11	--	37	--	66	--	67	--
<u>Japan</u> Coal tar distillate			11	200	23	1.607	78	1.668	96	1.683	--	--
<u>Humble, Baytown</u> Nuclear reactor coolant, (Low S)			10	200								

work and two 5-gallon cans retained by Humble [5]. One of these was supplied to Phillips for the work herein reported. It is believed this oil originated as a catalytic cracking heavy cycle, and that the special processing to which it was subjected comprised catalytic desulfurization and distillation.

No strictly lubricating oils fractions were examined.

1.4 Coal Tar Distillates

Two samples of coal tar middle oil distillates were obtained. One, obtained from Pittsburgh Coke and Chemical Company, should be typical of U. S. coking operations. The other was a Japanese sample, submitted for carbon black feed evaluation, but not identified as to exact source.

The data on properties and composition of the feed stocks are tabulated in Tables I and II.

2. PROCESSING METHODS

Fractional distillations were carried out on most of the materials submitted to obtain more desirable boiling ranges, or a series of such fractions from a single, wide range stock. Equipment used was standard glass laboratory equipment with fractionating columns of several types. Some distillations were carried out in small steel batch stills in the pilot plant area.

Solvent extractions were carried out in glass equipment by standard laboratory procedures.

Desulfurization and dealkylation were carried out in continuous flow equipment normally used in hydrocracking.

Thermal and radiation stability tests were carried out in apparatus devised for the purpose or for testing other types of coolants.

Detailed descriptions of the apparatus and procedures used for these processing steps and tests are given in the following section covering the various processes.

IV. EXPERIMENTAL STUDIES

1. STABILITY OF FUSED RING AROMATICS

As has been pointed out, several fused aromatic ring systems may occur in heavy cycle and extract oils and in coal tars. Lower boiling range materials contain substituted naphthalenes. Intermediate range materials (600 to 750°F normal boiling range) contain phenanthrenes and, in the case of coal tar, anthracenes. There are indications (NMR) that anthracene rings are in low concentration in heavy cycle oil from catalytic cracking of West Texas crude. Chromatography of hydrodealkylate indicated that pyrenes may be present in the heavier fractions of this material.

Several pure (unalkylated) ring compounds were tested for short term radiolytic and thermal stability to see if any certain ring systems need be eliminated from a coolant. Samples were irradiated under a linear electron accelerator (6 MeV) at 600 to 650°F to a dose of about 5×10^9 rads (about eight hours). The sample holders were aluminum or stainless steel and were outgassed and slightly pressurized with argon. Samples of terphenyl (Santowax OMP) were irradiated simultaneously and identically to determine dosage. Thermal stability was evaluated by heating three-gram samples in mild steel containers for 48 hours at 650 to 700°F. Gas and polymer production was measured to indicate degree of instability. Results of these tests are given in Table III and Figure 1 for radiolytic and thermal stability, respectively.

TABLE III

STABILITY OF SOME PURE FUSED RING COMPOUNDS TO 6-MEV ELECTRONS

Conditions: 600 to 650°F, 8 hr		
Sample	Rating Relative to Santowax OMP	
	High-Boiler Generation	Gas Generation
Naphthalene	0.4	---
Anthracene	0.9	2.0
Phenanthrene	0.8	0.8
Pyrene	0.9	---

Results indicated that naphthalene had excellent radiolytic and thermal stability. Anthracene was less stable than phenanthrene or pyrene. Only anthracene generated insoluble material. Coke was formed by anthracene during both thermal and radiolytic stability tests. Insoluble products were looked for but not found in the other samples. These results indicated that coal tars containing anthracenes would be less stable thermally than cycle and exact oils

rich in phenanthrenes or pyrenes. Alkyl naphthalenes are too low boiling for coolants except when highly alkylated, and this degree of alkylation reduces radiolytic stability. So the desirable compounds in a low cost coolant appeared to be phenanthrene, pyrene, and moderately alkylated phenanthrenes and pyrenes.

2. STABILITY OF VARIOUS STOCKS

A number of commercial stocks were tested for differences in thermal and radiolytic stability. Figure 2 shows the generation of high boiler and gas in 48 hours at various temperatures for three stocks: a Pittsburgh coal tar, a heavy cycle oil extract, and Humble nuclear reactor coolant. Figure 3 shows gain in viscosity during 65 hours at various temperatures and also gas generation. Table IV gives the relative radiolytic stabilities of a number of commercial stocks.

Fig. 2 Thermal stability of various stocks.

Fig. 1 Thermal stability of pure fused ring compounds.

Similar oil stocks from various sources differed surprisingly little in radiolytic and thermal stability. Coal tar had superior radiolytic stability but inferior thermal stability. Another surprising result was that the concentration of components in the oils and tars varied little during radiolytic and thermal stability tests in spite of conversions as high as 30 percent. In other words, highly unstable components were expected but not found to disappear during the tests. Gas chromatograms of samples before and after stability tests were almost identical. The rapid disappearance of a component was never observed.

3. DETERMINATION OF COMPOSITION OF STOCKS

Complexity of the oil and tar stocks even after fractionation precluded effective use of ultraviolet or infrared

Fig. 3 Thermal stability of various stocks.

TABLE IV

STABILITY OF VARIOUS STOCKS TO 6-MEV ELECTRONS

Conditions: 600 to 650°F, 8 hr.

Sample	Rating Relative to Santowax OMP	
	High Boiler Generation	Gas Generation
Pittsburgh coal tar	0.9	1.0
Japanese coal tar	0.9	1.0
Borger SO ₂ extract oil	1.5	10.0
D-X Sunray carbon black feed stock	1.9	11.0
Humble NRC (low S)	1.1	14.0
Esso aromatic concentrate (phenol extract)	1.2	13.0
Okmulgee decant oil	2.0	11.0
Great Falls slurry oil	1.6	5.0
Woods Cross syn. tower bottoms	2.0	15.0

adsorption spectroscopy. Proton magnetic resonance spectrometry was more successful and checked carbon-hydrogen and molecular weight measurements when samples were lightly alkylated. For example, Hydrodealklate A of an SO₂ extract of heavy cycle oil from West Texas crude (Borger SO₂ extract) was found to have the following population of protons:

on aromatic ring	0.75
on carbon adjacent to aromatic ring	0.17
on carbon nonadjacent to aromatic ring	0.06
unidentified	0.02

The sample was assumed to consist entirely of phenanthrene containing x methyl groups and y alkyl groups of n length per molecule. The three simultaneous linear equations representing populations of the first three types of protons (the unidentified protons were ignored) were solved to give x = 0.50 (average number of methyl groups per molecule), y = 0.30 and n = 2.0 (an average equivalent to 0.30 ethyl groups per molecule). The average C/H atomic ratio calculated from this solution was 1.24 and exactly checked the experimental value. The number average molecular weight calculated from this solution was 193, and compared favorably with the experimental value of 185.

The proton resonance spectra indicated that little anthracene was present in the predominantly phenanthrene composition. Gas chromatography of Hydrodealkylate A indicated that pyrene and lightly alkylated pyrenes also were present.

Table V lists the degrees of alkylation of several candidate coolants as obtained from their proton magnetic resonance spectra. The coal tar differs from the oils in having fewer higher alkyl groups. Irradiation of the dealkylated Okmulgee decant oil preferentially removed the larger alkyl groups. This is

TABLE V
DEGREE OF ALKYLATION OF COOLANTS BY NMR

Sample	Number and Length of Alkyl Groups		
	Methyl Groups, Number/Molecule	Higher Alkyl Groups Number/Molecule	Average Length
Pittsburgh coal tar	0.34	0.04	2.0
Dealkylated Okmulgee decant oil	0.67	0.27	6.0
Dealkylated or decant oil after e ⁻ irradiation (10 ⁹ rads)	0.65	0.18	5.6
Dealkylate (A) of Borger SO ₂ extract oil	0.50	0.30	2.0

consistent with poor radiolytic stability exhibited by highly alkylated stocks. The small average size of alkyl groups in Hydrodealkylate A compared to the dealkylated Okmulgee oil is probably due to fractionation performed by SO₂ extraction of the oil used as feed stock for Hydrodealkylate A.

4. PROCESSING OF COMMERCIAL STOCKS

Some of the commercial samples which have been discussed were then refined by hydrodesulfurization and hydrodealkylation in an attempt to improve radiolytic and thermal stability. Resulting products were distilled, and fractions in the desired boiling range (usually 650 to 750°F) were tested for stability. The objective of this phase was to determine if sufficient increases in stability could be obtained by these refining methods. The apparatus used for processing was continuous flow, pressurized equipment. This apparatus has been described in reports on hydrocracking studies.

4.1 Sulfur Removal

All feedstocks were subjected to catalytic hydrodesulfurization at conditions of 775 to 800°F, 1000 psig, 0.5 liquid hourly space rate (LHSV), and 0.8 standard cubic feet per hour hydrogen flow. The catalyst used in all runs was cobalt molybdate on alumina (G-59) which contained 3.0-percent cobalt and 5.9-percent molybdenum and had a surface area of 139 square meters per gram. Since the sulfur is present in these stocks as ring sulfur, the above relatively severe conditions were employed, and some ring saturation may have occurred. A summary of hydrodesulfurization tests is given in Table VI. Sulfur content of all charge stocks was reduced to less than 0.03 to 0.5 weight percent. All of the materials from refinery operation contained nitrogen in a low concentration of 0.04 to 0.10 weight percent. The nitrogen compounds present were quite refractory, and, in general, only about 50 percent removal was observed although sulfur removal was high in all runs. The two coal tars were higher in nitrogen (1.3 weight percent), and the hydrodesulfurization run gave a product containing 0.18 weight percent nitrogen. Samples which were not reduced in sulfur content to the desired level were recycled through the reactor to give products containing less than 0.03 weight percent sulfur.

Distillation data on hydrodesulfurized products indicated that some ring hydrogenation and hydrocracking occurred under the relatively severe conditions employed for sulfur removal. This was shown by change in boiling ranges and production of material boiling below 650°F and definite changes in the higher boiling components. These changes are shown in a typical distillation of hydrodesulfurized full range Phillips SO₂ extract in Table VII. Other evidence of ring saturation and hydrocracking was shown in carbon/hydrogen ratios and molecular weight data. For a given boiling range before and after hydrodesulfurization, molecular weights (average) were unchanged, but carbon/hydrogen atomic ratios were lowered (generally from 0.80 to 0.90 down to 0.75 to 0.80).

4.2 Hydrodealkylation

Two low sulfur stocks (Phillips SO₂ extract and Humble nuclear reactor coolant) were subjected to catalytic hydrodealkylation. Reaction conditions were 1000°F, 1000 psig, 0.5 to 1.0 LHSV, and 1.2 to 2.4 standard cubic feet per hour hydrogen flow. Chromia on alumina catalyst (R-129) was used in these tests

TABLE VI

HYDRODESULFURIZATION OF COMMERCIALY AVAILABLE FEEDSTOCKS

Sample Description	Boiling Range, (°F)	Sulfur Content(Wt%)	
		Before	After
Phillips [a] SO ₂ extract	500-900	1.4	< 0.03
Phillips [a] SO ₂ extract	575-605	0.8	< 0.03
Phillips [a] SO ₂ extract	640-670	1.2	< 0.03
Phillips [a] SO ₂ extract	670-690	1.4	< 0.03
Phillips [a] SO ₂ extract	690-730	1.5	< 0.03
Phillips SO ₂ extract [b]	640-750	3.1	0.07
Esso aromatic concentrate	690-780	1.8	0.11
Esso aromatic concentrate [c]	690-780	0.11	< 0.03
D-X Sunray furnace-black feedstock	740-780	0.96	< 0.03
Pittsburgh coal tar	620-660	0.69	< 0.05
Pittsburgh coal tar	660-690	0.60	< 0.05
Conditions: 775-800°F			
1000 psig			
0.5 LHSV			
0.8 SCFH hydrogen flow			

- [a] From Borger, Texas Refinery
 [b] Dimethylsulfoxide extract of SO₂ extract
 [c] Second pass through reactor

TABLE VII

BOILING RANGE OF SO₂ EXTRACT OIL BEFORE AND AFTER HYDRODESULFURIZATION

Distillation Boiling Range	Borger Extract (Full Range)(Wt%)	Hydrodesulfurized Extract(Wt%)
0-650°F	10.4	24.2
650-750°F	35.2	52.8
750-850°F	47.1	17.9
850°F +	7.3	5.1

(13.7 percent chromium and 100 square meters per gram). After hydrodealkylation each product was distilled under vacuum to give a 650 to 750 °F fraction which gave stocks for comparison with the same boiling range material before and after each stage of refinement. Most of the hydrodealkylations were made on the hydrodesulfurized Phillips SO₂ extract (either 600 to 800 °F or 650 to 850 °F fractions). Typical distillation data for preparation of a 650 to 750 °F cut from hydrodealkylation of a 650 to 850 °F fraction are shown in the following tabulation:

<u>Boiling Range</u>	<u>Wt %</u>
0 to 500 °F	45.7
500 to 650 °F	11.2
650 to 750 °F	29.3
750 °F +	13.8

These data indicated a large yield of lower boiling material which could be attributed to two factors: long contact time in the reactor and high initial activity of the catalyst. The latter may have contributed more since all runs were short and "lined out" activity had not been attained. However, it should be pointed out that the main purpose of these initial tests was to prepare highly aromatic, three-ring stocks for stability tests. Conditions for optimum yields would be developed later if the product were found to be more stable than the virgin stocks. The low boiling fraction (0 to 500 °F) contained a large amount of naphthalene and methylnaphthalenes (425 to 500 °F range). Properties of the dealkylated Phillips and Humble stocks are given in Table VIII. Hydrodealkylate Samples A and C (Phillips) were light yellow solids (at room temperature); all other samples were semi-solids, yellow to light brown in color.

TABLE VIII
 PROPERTIES OF COMMERCIAL STOCKS AFTER
 HYDRODESULFURIZATION AND HYDRODEALKYLATION

	<u>C/H Ratio</u>	<u>Molecular Weight, No. Avg.</u>
<u>Phillips Borger SO₂ Extract (650 to 750 °F)</u>		
Raw extract	0.73	227
Hydrodesulfurized	--	223
Hydrodealkylated Sample A	1.24	185
Hydrodealkylated Sample B	1.18	188
Hydrodealkylated Sample C	1.18	188
<u>Humble Nuclear Reactor Coolant (low S)</u>		
670 to 750 °F fraction	0.73	231
750 to 850 °F fraction	0.82	253
Hydrodealkylated, 650 to 750 °F	1.20	219

4.3 Characterization of Refined Products

Since all stocks in this investigation are complex and of various boiling ranges, all identifications were of a qualitative nature. Molecular weight and carbon/hydrogen data were used for characterization of fractions in the same boiling range. Although all stocks were too complex for good resolution by gas chromatography, it is possible to see some structural changes. Four column packings were tested for obtaining qualitative data:

20% Apiezon L on Chromosorb W

20% Carbowax on Chromosorb P

20% Silicone SE 30 on Chromosorb P

20% Lithium chloride on Chromosorb P

Of the first three listed, the Carbowax column gave the best resolution, but it was limited to a maximum temperature of 250°C. The lithium chloride column was selected for most of the chromatographic work since high column temperature was possible (up to 450°C) and elution times were considerably shorter. Fairly good chromatographic data were obtained on some Pittsburgh coal tar fractions using the lithium chloride column. Chromatograms of two of these cuts (620 to 660°F and 690 to 740°F) were good enough to show that one fraction contained mainly three ring aromatics compared to a higher boiling cut of four ring aromatics.

Gas chromatograms were quite useful in observing structural changes in 650 to 750°F fractions of the Phillips SO₂ extract after the two stages of refining. The raw extract gave a chromatogram of at least 23 peaks with very poor resolution. The hydrodesulfurized stock showed a similar pattern except that elution temperatures were generally shifted to lower values. The hydrodealkylated product was quite different from the above samples; five major peaks were observed which made up about 90 percent of the sample. Two of these were phenanthrene and anthracene with the other two major components eluting at the same time and temperature as pyrene. Similar chromatographic data were obtained for the Humble stock before and after hydrodealkylation. Nuclear magnetic resonance data for hydrogen distribution were obtained for the above samples. The most striking observation in this analysis was that the aromatic hydrogen contents of raw, hydrodesulfurized, and hydrodealkylated samples were 17, 13, and 75 percent, respectively. Although these samples were too complex to determine the exact structures present, hydrogen types present were identified. For the hydrodealkylated sample, an average structure could be postulated as a methylphenanthrene (only a small quantity of anthracene was shown in the NMR spectra).

Further analytical work could establish the structures present in the hydrodealkylated sample.

4.4 Radiolytic Stability

Radiolytic stability tests were performed on some of the stocks described in this report. Electron irradiations under a Linac were at 650°F for eight hours to total dosages of 6 to 8 x 10⁹ rads. Polymer formation was determined by a microsublimation technique, and values for polymer and gas production were compared with terphenyls (Santowax OMP control). Results of radiolysis tests on samples of raw and refined Phillips aromatic stocks (650 to 750°F) are shown

in Table IX which gives polymer formation, radiolytic gas, and molecular weight changes. These data indicated that hydrodealkylation greatly improves stability. Polymer values were about 1/3 those found for the raw extract oil; gas values were about 1/5. Compared to Santowax OMP, relative polymer values for the dealkylated samples were in the range 0.57 to 0.70. Hydrodesulfurized samples were only slightly improved over the raw extract oil.

TABLE IX
COMPARISON OF RADIOLYTIC STABILITIES OF REFINED
PHILLIPS (BORGER REFINERY) AROMATIC STOCKS

<u>Phillips Extract (650-750°F)</u>	<u>Relative Polymer [c]</u>	<u>Radiolytic Gas (cc/W-hr)</u>	<u>Average Molecular Wt</u>	
			<u>Before</u>	<u>After</u>
Raw Extract [a]	1.7	3.4	227	273
Raw Extract (690-730°F) [b]	1.4	1.6	-	-
Hydrodesulfurized [a]	1.4	0.9	223	278
Hydrodesulfurized [b]	1.2	4.0	223	256
Hydrodealkylated (A) [a]	0.60	0.6	185	229
Hydrodealkylated (A) [b]	0.52	3.0	185	213
Hydrodealkylated (B) [a]	0.70	0.5	188	209
Santowax OMP [a] (control)	1.0	0.10	230	258
Santowax OMP [b] (control)	1.0	0.07	230	290

[a] 5.6×10^9 rads dosage

[b] 8.3×10^9 rads dosage

[c] Relative to Santowax OMP run simultaneously.

Radiation tests on hydrodesulfurized commercial stocks (other than Phillips) are summarized in Table X. The Pittsburgh coal tar sample (620 to 660°F) showed the best stability (0.6 to 0.8 relative to Santowax OMP). The lower boiling Humble nuclear reactor coolant (670 to 750°F) and the Esso aromatic stock were quite similar. Although comparable data on virgin stocks are not available for the same boiling ranges reported here, it is apparent that sulfur removal improves radiolytic stability slightly.

A combination of sulfur removal and hydrodealkylation processing of aromatic stocks available from refinery streams resulted in a 650 to 750°F range product of mainly three ring aromatics which was relatively stable toward radiolysis. Hydrodesulfurization alone resulted in only slight improvements on radiolytic stability.

TABLE X

RADIOLYTIC STABILITY OF HYDRODESULFURIZED COMMERCIAL STOCKS

	Relative Polymer [c]	Radiolytic Gas (cc/W-hr)	Average Molecular Wt	
			Before	After
Santowax OMP [a] (control)	1.0	0.10	230	258
Santowax OMP [b] (control)	1.0	0.07	230	290
Humble NRC (670-750°F) [b]	0.76	1.5	231	278
Humble NRC (750-850°F) [a]	1.2	2.0	253	284
Humble NRC (750-850°F) [b]	1.3	1.5	253	278
Esso aromatic concentrate (650-750°F) [b]	0.87	1.9	232	249
Pittsburgh coal tar (620-660°F) (620-660°F) [a]	0.83	0.60	199	215
Pittsburgh coal tar (620-660°F) [b]	0.61	0.10	199	215
[a] 5.6×10^9 rads dosage				
[b] 8.3×10^9 rads dosage				
[c] Relative to Santowax OMP run simultaneously.				

4.5 Thermal Stability

Testing of the refined samples for thermal stability was carried out in equipment revised from that reported earlier. Test cells of stainless steel were used under 200 pounds per square inch nitrogen pressure (at room temperature). A drawing of the assembled cell is shown in Figure 4. Five-gram samples were used in these tests with a thermowell extending below the surface of the sample. By use of nitrogen pressure and proper insulation, no condensation occurred in the top part of the cell. Samples were analyzed for high boiler content by microsublimation, and molecular weights of the thermally treated samples were determined. Temperatures used in this series of tests were 650 , 700 , 740 , and 750°F. A tabulation of typical results is given in Table XI. Results from the thermal tests showed larger differences in stabilities than did the radiolytic tests. Hydrodesulfurization and hydrodealkylation greatly improved thermal stability of comparable boiling range stocks. The effect of processing Phillips SO₂ extract is shown in Figure 5. At 750 °F only 5 percent high boiler formed from hydrodealkylated stock compared to 71 percent from the raw extract. Pittsburgh coal tar, which gave disappointing thermal results, was greatly improved by hydrodesulfurization as shown in Figure 6. Chromatographic analysis showed this stock to be quite similar to the hydrodealkylated Phillips extract, and these data show similar thermal stability values. Data for all of the refined commercial stocks are shown in Figure 7. The hydrodealkylated Humble nuclear reactor coolant was the least stable of those tested and quite similar to the hydrodealkylated Okmulgee decant oil. The Pittsburgh coal tar

Fig. 4 Stainless steel cell for thermal stability experiments.

TABLE XI

DATA FROM THERMAL STABILITY TESTS ON REFINED COMMERCIAL STOCKS

Sample	High Boiler Formed (Wt%)			
	650°F	700°F	740°F [b]	750°F
Borger SO ₂ extract [a]	1.2	7.7	30.2	71.0
Desulf., Dealk. Borger extract [a]	0.1	0.6	4.2	4.8
Desulf. Pittsburgh coal tar (620-660°F)	1.0	2.2	6.9	8.7
Dealk. Humble NRC [a]	1.7	4.8	20.2	26.0
Sample	Molecular Weights			
	Before	650°F	700°F	750°F
Borger SO ₂ extract [a]	227	235	240	--
Desulf., Dealk. Borger extract [a] (B)	188	197	194	199
Desulf. Pittsburgh coal tar (620-660°F)	199	206	208	214
Dealk. Humble NRC [a]	219	234	231	261
[a] 650-750°F fractions				
[b] Temperature reported fluctuated from 735°F to 750°F.				

was the only hydrosulfurized sample tested using the revised thermal stability test method.

Gas production was followed by pressure readings on each sample. With each sample initially under 200 psig nitrogen pressure (80°F), the test cell pressure increased rapidly to 400 to 440 psig when placed in the heated aluminum block. Pressure readings were then taken periodically during the tests. Pressure increases with time are shown in Figure 8 for the 700 °F run and in Figure 9 for the 750 °F run. These data were consistent with high boiler and molecular weight data. For the refined samples, pressure leveled off after the first half of the test. This was an indication that any alkyl groups remaining on the treated samples were dealkylated leaving the more stable three and four ring aromatics. Pressure over all samples at 650 °F remained almost constant (little gas formed) and are not shown here.

Fig. 5 Effect of refining on thermal stability of Phillips extract oil.

Fig. 6 Effect of hydrodesulfurization on thermal stability of Pittsburgh coal tar.

Fig. 7 Thermal stability data for refined commercial stocks.

Fig. 8 Thermal stability tests showing pressure buildup in test cells at 700°F.

Fig. 9 Thermal stability tests showing pressure buildup in test cells at 750°F.

V. CONCLUSIONS

Hydrodealkylated heavy cycle oil fractions and hydrodesulfurized coal tar oil fractions are promising candidate moderator coolants for nuclear power reactors. Small scale static tests indicate that they have satisfactory physical properties and radiolytic and thermal stability for the indirect steam power cycles under consideration for nuclear power reactors. The present economic value of the aromatic feed stocks is low, near one cent a pound. Processing costs would strongly depend on the size or scale of operations. A reasonably sized commercial process should produce such coolants for sale under five cents a pound.

This report has attempted to summarize the status of low cost moderator coolants. For greater details the reader is invited to the quarterly reports of this project referenced in Table XII.

TABLE XII

REFERENCES FROM QUARTERLY REPORTS

Information	QR No.	Report No.	Page
Apparatus and procedures			
Thermal stability	1	IDO-16675	32-35
" "	1	IDO-16675	24-25
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	5	IDO-16761	55-58
	6	IDO-16787	46
	7	IDO-16807	39-41
	9	IDO-16869	50-51

VI. REFERENCES

1. Private communication, H. J. Gercke, Atomics International, to J. C. Hillyer, August 18, 1959.
2. Proceedings of the Organic Cooled Reactor Forum, October 6-7, 1960, NAA-SR-5688 (December 1960).
3. Annual Technical Progress Report, AEC Unclassified Programs, Fiscal Year 1961, NAA-SR-6370 (August 15, 1961).
4. Annual Technical Progress Report, AEC Unclassified Programs, Fiscal Year 1962, NAA-SR-7400 (November 15, 1962).
5. Private communication, H. G. Corneil, Humble Oil and Refining, Baytown, Texas, to L. V. Wilson.
6. J. G. Carroll, Petroleum Refinery Streams as Prospective Reactor Coolants: Thermal Stability Investigations, TID-6367 (May 31, 1960).
7. R. O. Bolt et al, Radiation Stability of Organic Fluids. California Research - AEC Report No. 17 Progress Report, April 1 to June 30, 1962, TID-16999 (September 21, 1962).
8. Private communication, W. H. Yanko, Monsanto Research Corp., to J. C. Hillyer, July 26, 1961.
9. E. F. Baxter Jr. and J. F. Black, The Application of Petroleum Products as Moderator-Coolants in Marine Propulsion Reactors, ESSO-MA-3 (August 1, 1959).
10. W. W. West, The Radiolysis of Prospective Organic Reactors Coolants, Report No. 13, AECU-4295 (August 13, 1959).
11. A. N. Sachanen, The Chemical Constituents of Petroleum, Reinhold, New York (1945).
12. F. D. Rossini et al, Hydrocarbons from Petroleum, Reinhold, New York (1953).

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